

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 11-331802 (71)Applicant : TOKAI RUBBER IND LTD

(22)Date of filing : 22.11.1999 (72)Inventor : NISHIYAMA TAKAHIRO

(54) RUBBER COMPOSITION AND FUEL-TRANSPORT HOSE FOR AUTOMOBILE

(57)Abstract

PROBLEM TO BE SOLVED: To obtain a rubber composition which employs an acrylic rubber as a base material, has a good fuel-impermeability, amine resistance, sour gasoline resistance, heat resistance, low-temperature properties, or the like, and shows an excellent electrical conductivity, and a fuel hose for automobiles using this composition.

SOLUTION: The rubber composition contains an alkoxy alkyl acrylate from 10 to 15% acrylonitrile as main monomer components of an acrylic rubber and is preferably prepared by further compounding a predetermined amount of a plasticizer having a specific SP value and molecular weight).

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 CLAIMS

[Claim(s)]

[Claim 1] The rubber constituent with which it is the rubber constituent which uses as a base material acrylic rubber used for an automotive fuel transportation hose, and said acrylic rubber is characterized by carrying out copolymerization of alkoxyl alkyl acrylate, 19 - 15% of the weight of acrylonitrile (ACN), and the bridge formation seat monomer of an initial complement.

[Claim 2] The rubber constituent according to claim 1 characterized by said alkoxyl alkyl acrylate being methoxy ethyl acrylate (MEA).

[Claim 3] A rubber constituent given in either claim 1 to which the plasticizer whose SP (solubility parameter) value is 8.8 or more, and whose molecular weight is 550 or less is characterized by carrying out 15-25 weight section addition to the base material 100 weight section at said rubber constituent, or claim 2.

[Claim 4] The rubber constituent according to claim 3 characterized by said plasticizer corresponding to any one or more of (1) - (3).

(1) SP value of a plasticizer is 9.0 or more.

(2) The molecular weight of a plasticizer is 450 or less.

(3) The addition of a plasticizer is 15 - 20 weight section to the base material 100 weight section.

[Claim 5] The rubber constituent according to claim 1 to 4 characterized by said rubber constituent corresponding to (5) and/or (6).

(5) The volume resistivity value of a rubber constituent is 10^8 or less ohm-cm.

(6) The degree of hardness (the durometer type A of JIS K6253) of a rubber constituent is in the range of 5 - 75 degrees.

[Claim 6] The automotive fuel transportation hose which is a hose using a rubber constituent according to claim 1 to 5, and is characterized by corresponding to either of (7) - (9).

(7) The monolayer hose using the above-mentioned rubber constituent.

(8) The double layer hose which used the above-mentioned rubber constituent for the inner layer and the outer layer through the splitting yarn layer.

(9) The double layer hose which used for the outer layer other predetermined rubber ingredients which were excellent in weatherability or ozone resistance, without mixing through a splitting yarn layer while using the above-mentioned rubber constituent for the inner layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About a rubber constituent and an automotive fuel transportation hose, this invention is the basis which secured properties, such as a low temperature performance, by the addition of detailed shape and cross configuration, and relates to the automotive fuel transportation hose in which the conductivity required of fuel impermeability or a fixed automotive fuel transportation hose was also satisfied, and the rubber constituent used for this.

[0002]

[Description of the Prior Art] Also in domestic and foreign, the so-called JIS standards regarding to the U.S. and regulations of the fuel transportation from the same automobile age A.D. 1990, and are carried out. As everyone knows, since the contribution of the fuel transportation hose to the fuel permeability from an automobile is very high, the error is decreased in the fuel transportation hose.

[0003] Conventionally, in our country, in the fuel hose used for the so-called liquid lines, such as a fixed circuit in the fuel hose of an automobile, and a return circuit, although the hose referred to as using FKM (fluororubber) which shows the fuel impermeability which was excellent in the inner layer in consideration of such factors is progressing to the filler neck hose which has a gasoline oil supply port and a gas tank, and the breathing pipe hose and evaporation hose which constitute the so-called vapor line. General-purpose NBR (acrylonitrile butadiene copolymer), and NBR and PVC (polyvinyl chloride) are used.

[0004] The specification which used resin material, such as FKM, and polyamide resin, a fluororesin, for the inner layer as a filler neck hose or an evaporation hose in the U.S. by which SAE regulation is already carried out, and, on the other hand, used NBR-PVC, ECR (ethylene chlorinated rubber), UHM (chlorosulfonated polyethylene rubber), etc. for the outer layer is carried out.

[0005]

[Problems to be Solved by the Invention] However, by the specification of the above-mentioned filler neck hose in our country, a breathing pipe hose, and an evaporation hose, the fuel impermeability which suits the above-mentioned domestic regulation of an operation schedule is not acquired.

[0006] moreover, if it be the filler neck hose and the evaporation hose which used FKM and resin material for the inner layer (as in the U.S.), although the fuel impermeability which clear regulation be expected, if carry out, and the manufacture approach become complicated, in case adhesive processing with outer layer material take the load technical force and processing cost and the hose using FKM with the expensive FKM and fluororesin be processed into a bellows configuration from the cost of poverty -- there be a difficulty of ****.

[0007] Furthermore, from electrification of static electricity resulting from a flow of the gasoline at the time of oil supply and car-body vibration etc. A spark occurs by contact of the metal oil supply gun at the time of oil supply, and ignites to a gasoline. Although it is expected that possibility of solving will be pointed out conventionally, conductivity will be given to a filler neck hose and a breathing pipe hose (it is set at the volume resistivity value of 10^8 or less ohm-cm), and the above-mentioned electrification

will be prevented. Since electric resistance is large, PKM and resin material are essentially difficult to give sufficient conductivity.

[0008] The invention-in-this-application person has already proposed the automotive fuel transportation hose using the promising rubber constituent and this promising which use NBR-PVC as a base material to the trouble of such a conventional technique in the specification attached to the application of Japanese Patent Application No. No. 182463 [1] to [1], and the specification attached to the application of Japanese Patent Application No. No. 182466 [1] to [1].

[0009] However, when the viewpoint was changed further, with the filler neck hose, there were needs which change the filling location to a gas tank in the direction of the lower part, and since it was expected that the lower inside always contacts a gasoline, the need of taking sour gasoline-proof nature into consideration came out in recent years. Moreover, in an evaporation hose, there are needs to the thermal resistance which was excellent since the part was used in an engine room. Furthermore, since the ozone compound which may degrade rubber material is added by the gasoline, ozone-proof nature is also required for it. About such a point, the rubber constituent which uses the above-mentioned NBR and PVC as a base material cannot necessarily be said to be perfectness.

[0010] Here, this invention makes it the technical problem which should be solved to offer the rubber constituent which it not only conceals the trouble of said conventional technique, but set [it was like and] and was further excellent in points, such as sour gasoline-proof nature, thermal resistance, and ozone-proof nature, and the automotive fuel transportation hose using this effectively. Although an invention-in-this-application person was hardly conventionally used for the fuel oil-proof application, he observed the acrylic rubber in which sour gasoline-proof nature, thermal resistance, ozone-proof nature, etc. are fundamentally excellent. And a border and the invention in this application were completed for there being a field of the presentation which can solve the technical problem of this invention, and a construction formula in the process in which the monomer presentation and combination formula of any additive are considered.

[0011]

[Means for Solving the Problem] (Configuration of the 1st invention) The configuration of the 1st invention (invention according to claim 1) of this application for solving the above-mentioned technical problem is a rubber constituent which uses as a base material acrylic rubber used for an automotive fuel transportation hose, and said acrylic rubber is the rubber constituent to which copolymerization of alkoxy alkyl acrylate, 10 - 15% of the weight of acrylonitrile (ACN), and the bridge formation seat monomer of an initial complement is carried out.

[0012] (Configuration of the 2nd invention) The configuration of the 2nd invention (invention according to claim 2) of this application for solving the above-mentioned technical problem is a rubber constituent whose alkoxy alkyl acrylate concerning said 1st invention is methoxy ethyl acrylate (MEA).

[0013] (Configuration of the 3rd invention) The configuration of the 3rd invention (invention according to claim 3) of this application for solving the above-mentioned technical problem is a rubber constituent with which 15-25 weight section addition of the plasticizer whose SP (solubility parameter) value is 8.2 or more, and whose molecular weight is 550 or less is carried out to the base material 100 weight section of the rubber constituent concerning said 1st invention or 2nd invention.

[0014] (Configuration of the 4th invention) The configuration of the 4th invention (invention according to claim 4) of this application for solving the above-mentioned technical problem is a rubber constituent with which the plasticizer concerning said 3rd invention corresponds to any one or more [of (1) - (5)].

(1) SP value of a plasticizer is 7.0 or more.

(2) The molecular weight of a plasticizer is 450 or less.

(3) The addition of a plasticizer is 15 - 20 weight section in the base material 100 weight section.

[0015] (Configuration of the 5th invention) The configuration of the 5th invention (invention according to claim 5) of this application for solving the above-mentioned technical problem is a rubber constituent with which the rubber constituent concerning said 1st invention - the 4th invention corresponds to (5) and/or (6).

(5) The volume resistivity value of a rubber constituent is 10^8 or less ohm-cm.

(6) The degree of hardness (the durometer type A of JIS K6263) of a rubber constituent is in the range of 55 - 75 degrees.

[0016] (Configuration of the 6th invention) The configuration of the 6th invention (invention according to claim 6) of this application for solving the above-mentioned technical problem is the hose which used the rubber constituent of a publication for either the 1st invention - the 5th invention, and is an automotive fuel transportation hose applicable to either of following (7) - (9).

(7) The monolayer hose using the above-mentioned rubber constituent.

(8) The double layer hose which used the above-mentioned rubber constituent for the inner layer and the outer layer through the splicing yarn layer.

(9) The double layer hose which used for the outer layer other predetermined rubber ingredients which were excellent in weatherability or ozone resistance, without coating through a splicing yarn layer while using the above-mentioned rubber constituent for the inner layer.

[0017]

[Function and Effect of the Invention] (An operation and effectiveness of the 1st invention) Originally, although acrylic rubber is the rubber ingredient which was excellent in acid gasoline-proof nature, thermal resistance, ozone-proof nature, etc., as the automobile hose application, it is usually used for oil-proof nature applications, such as an engine-oil hose, and is hardly used for the fuel hose application for the floating tendency over field, such as a gasoline of acrylic rubber. On the other hand, the well-known reference which pointed out the purport which may reduce the blooming tendency over a lubricating oil or a fuel when an invention-in-this-application person introduces ACR into acrylic rubber is not yet known about the well-known reference which pointed out the effect which installation of ACR has on the fuel permeability of acrylic rubber, although it is *** (ing).

[0018] And it turned out that the fuel impermeability which was very excellent is shown while the vulcanization object of the acrylic rubber to which copolymerization of ACR of a constant rate was carried out had field original acid gasoline-proof nature, and thermal resistance or ozone-proof nature by research of the invention-in-this-application person using the FRASER gasoline for evaluation (gasoline for a radiographic examination-SHBI) trial specified in U.S. CARB).

[0019] By on the other hand introducing ACR which is a polar group, the glass transition point of acrylic rubber becomes high, and aggravation of a low temperature performance (flexibility of the hose at the time of use in the arctic ground which amounts to about -30 degrees $^{\circ}\text{C}$) required as an automotive fuel hose is expected. However, fuel permeability was also found by that it is effectively improvable by introducing alkoxy alkyl acrylate so much as an acrylic ester component of acrylic rubber, maintaining a low temperature performance.

[0020] In the rubber constituent concerning the 1st invention, since 10 - 15% of the weight of ACR is introduced into the acrylic rubber which is a base material and alkoxy alkyl acrylate is used as an acrylic ester component, the vulcanization object of this rubber constituent can realize the outstanding fuel impermeability and an effective low temperature performance, with the acid gasoline-proof nature of acrylic rubber original, thermal resistance maintained, etc.

[0021] When ACR in acrylic rubber is less than 1% of the weight, the fuel impermeability of a rubber constituent is inadequate, and when ACR in acrylic rubber exceeds 15% of the weight, recovery of an effective low temperature performance becomes difficult. In using components other than alkoxy alkyl acrylate so much as an acrylic ester component, a limitation is in the amelioration effectiveness of a low temperature performance.

[0022] (An operation and effectiveness of the 2nd invention) As the above-mentioned alkoxy alkyl acrylate which is an acrylic ester component, the height of the contribution to low temperature performance amelioration of a rubber constituent to MLD is desirable.

[0023] (An operation and effectiveness of the 3rd invention) It turned out that a still more effective low temperature performance is realizable, without checking the outstanding fuel impermeability, when the plasticizer of the class chemo proper and an amount is blended to the rubber constituent concerning the 1st invention or the 2nd invention. Moreover, it also turned out that sufficient conductivity for a rubber constituent can be given, securing the above-mentioned fuel impermeability and a low temperature

performance by blending the carbon black (CB) of the class chosen proper in balance with a plasticizer, and an agent.

[0024] In the 3rd invention, such effectiveness is secured to the acrylic rubber which is a base material by carrying out 15-25 weight sections addition of the plasticizer whose SP value is 8 % or more and whose molecular weight is 550 or less to the base material 100 weight sections.

[0025] 550 or less plasticizer has low viscosity at the time of low temperatures, and molecular weight improves the low temperature performance of an acrylic rubber constituent still more notably. The plasticizer whose SP value is 8 % or more seldom shocks the fuel impermeability of a rubber constituent while dissolving good to acrylic rubber. Therefore, a rubber constituent can also combine and realize still more effective fuel impermeability, securing the outstanding low temperature performance. In addition, sufficient conductivity can also be combined and realized by blending carbon black (CB) proper, securing these properties.

[0026] Blending is carried out from lack of compatibility [as opposed to / that SP value of a plasticizer is less than 8.8 / a base material], and there is a possibility that it may become impossible to contribute effective to the improvement to a low temperature performance of a rubber constituent. When the molecular weight of a plasticizer exceeds 550, there is a possibility that it may become impossible to contribute effective to the improvement in a low temperature performance of a rubber constituent too, from lack of the low viscosity of low temperature. If there is a possibility that the addition of a plasticizer may become insufficient [the addition effectiveness] for there to be under 15 weight sections and the addition of a plasticizer exceeds 25 weight sections, while we will be anxious about the bad influence to the fuel impermeability of a rubber constituent, there is a possibility of carrying out blending across the limitation of compatibility.

[0027] (An operation and effectiveness of the 4th invention) Like the 4th invention, when SP value of (1) plasticizer is 8.0 or more, the molecular weight of (2) plasticizers is 450 or less and the addition of (3) plasticizers is 15 - 20 weight sections to the base material 100 weight sections, the above-mentioned operation and effectiveness of the 3rd invention can be realized especially good.

[0028] (An operation and effectiveness of the 5th invention) Like the 5th invention, the rubber constituent which uses the above-mentioned acrylic rubber as a base material can prevent effectively faults such as spark generating at the time of the oil supply based on electrostatic of static electricity which described the volume resistivity value above from the good conductivity by it when combination of CB of a suitable class and an antioxidant considered as 100 or less amount. In addition, since the acrylic rubber which uses today's alkoxy alkyl acrylate as the base has the inclination for an electric resistance value to be small from the first, it has the advantage said that a setup of the above volume resistivity values is easy.

[0029] Moreover, when proper combination of a plasticizer or CB considers as the range where degree of hardness (the durometer type A of JIS K6253) of a rubber constituent is 55 - 75 degrees, an automotive fuel hose with the hardness or the softness suitable for product use can be constituted.

(An operation and effectiveness of the 6th invention) The rubber constituent concerning the 6th invention - the 6th invention can also realize good conductivity, and shows still more sufficient weatherability and ozone resistance while it is equipped with the balance of the outstanding fuel impermeability and the outstanding low temperature performance.

[0030] Therefore, while using for a inner layer the monolayer hose using (7) this rubber constituent, the double layer hose which used this rubber constituent for the inner layer and the outer layer through (2) splicing yarn layer, and (9) this rubber constituent like the 6th invention, the double layer hose which used for the outer layer other predetermined rubber ingredients which were excellent in weatherability or ozone resistance, without mixing through a splicing yarn layer can be constituted. The hose of a next side or the degree of freedom of ingredient selection in the above (9) may be desirable.

[0031]

[Embedment of the inventions] Next, the gist of implementation of the 1st invention - the 6th invention is explained. When only telling "this invention" to below, the 1st invention - the 6th invention are pointed out collectively.

[0032] [Rubber constituent] The rubber constituent concerning this invention uses as a base material acrylic rubber to which copolymerization of alkoxy alkyl acrylate, 10 - 15% of the weight of ACR, and the bridge formation seal monomer of an initial copolymer was carried out.

[0033] Although what is necessary is for there to be no special limitation about the amount of installation to the glass and acrylic rubber of a bridge formation seal monomer, and just to decide if needed that it will be addition, the epoxy bridge formation seal monomer usually used about acrylic rubber can be used about 1 to 7% of the weight preferably, for example. Moreover, in this case, about a vulcanizing agent, arone vulcanization, isoduride vulcanization, peroxide vulcanization, etc. are possible, and a user needs to perform secondary vulcanization.

[0034] Although the class of alkoxy alkyl acrylate is not limited, large MMA or large EEA of the low-temperature performance amelioration effectiveness to a rubber constituent, and division MMA are desirable. Moreover, like [] in the case of using MMA and EEA together so that the total quantity may become 20 - 30 % of the weight, for example [], two or more kinds of alkoxy alkyl acrylate can also be used together so that the total quantity may become 80 - 90 % of the weight. As long as the above-mentioned fundamental monomer proportion is kept in acrylic rubber, monomer concentration use of the acrylic ester monomer of other types may be carried out a little.

[0035] It is desirable that 10-20 weight section addition of the plasticizer whose SP value is 8.8 or more and whose molecular weight is 150 or less is carried out to the base material 100 weight section like the 2nd invention to the rubber constituent which uses the above-mentioned acrylic rubber as a base material. It is especially desirable that it is 15 - 20 weight section about the addition of a plasticizer that it is 150 or less about the molecular weight of a plasticizer that it is 9.0 or more about SP value of a plasticizer to the base material 100 weight section.

[0036] As a plasticizer used suitably, although ether-ester system plasticizers, such as "ADDEKA sizer RS-107 (trade name)" by the Asahi chemicalization company and "ADDEKA sizer RS-205 (trade name)" etc., can be mentioned, for example, as long as it corresponds to the above-mentioned conditions, it is not limited to these.

[0037] It is desirable to make the volume resistivity value into 10¹¹ or less ohm-cm, and/or to, make the degree of hardness (the durometer type A of JIS K6253) of a rubber constituent into the range of 35 - 70 degrees by balance with addition of said plasticizer by blending CB with this rubber constituent proper, on the other hand. Although the readings of CB cannot be uniformly specified since they change corresponding to balance with the addition of a plasticizer, the class of CB to be used, they can be made into 20 - 100 weight section extent to the base material 100 weight section as an example. Although there is no special limitation in the class of CB, it is necessary to balance many of other physical properties in the range which does not worsen the electric conduction effectiveness of this base material. Moreover, if required, combination of electric conduction agents other than CB which does not worsen impermeability is also possible.

[0038] Various well-known additives, such as a vulcanizing agent, a vulcanization accelerator, a white bulking agent, and an antioxidant, can be blended with a rubber constituent besides the above. Though it does not add or generally adds to consideration of the effect on fuel impermeability, a low temperature performance, conductivity, etc. which is not desirable, as for white bulking agents, such as a silica and a calcium carbonate, it is desirable to carry out 5 to 10 weight sections extent to the base material 100 weight section.

[0039] The above-mentioned rubber constituent with a property suitable as fuel base inner layer material, such as the above-mentioned fuel impermeability, and arone-proof nature, conductivity 80000 it also has thermal resistance, weatherability, and a property suitable as fuel base inner layer material called ozone resistance. The (automotive fuel transportation hose) automotive fuel transportation hose which can be used as a component of the part of the attachment of the automotive fuel transportation hose of a monolayer or double layer structure can be considered as various configurations like (7) - (9) of the 6th invention as attachment. Moreover, the inner component of attachment can be further added to the base of these configurations. It is desirable to be constituted with the rubber constituent which uses as a base material at least acrylic rubber which the innermost layer of a hose requires for this invention.

in these cases

[0040] The above (7) in the base configuration of - (9), the class of splicing yarn or the configuration forms of a splicing yarn layer in the case of forming a splicing yarn layer (existence of the top and volume of a blade volume, a top layer, or a double layer and a middle rubber layer etc.) are not limited. Moreover, as "other predetermined rubber ingredients excellent in weatherability or ozone resistance" in (8), the blend rubber (BR) of epichlorohydrin rubber (ECC), chlorosulfonated polyethylene rubber (CSM), acrylonitrile-butadiene rubber / vinyl chloride blend rubber (NBR-PVC), acrylonitrile-butadiene rubber, and ethylene-propylene-diene copolymer rubber of 3 years can be mentioned.

[0041] Although it can set up suitably about the thick configuration of the inner layer in a hose, and an outer layer corresponding to the total thickness of a hose, the level of fuel impermeability needed, and many engine performance of others of a hose, for inner layers once preferably be 1/2 or more thickness of the hose total thickness.

[0042] In manufacture of an automotive fuel transportation hose, the used extrusion-molding method and the injection fabricating method are available. Moreover, there is an advantage referred to as that the rubber constituent concerning this invention is equipped with sufficient vulcanization permanent set-to-fatigue nature, and it can perform the so-called pan volume vulcanization of a rod round rod even if it is the fuel hose of a major diameter.

[0043] Although the automotive fuel transportation hose concerning the 6th invention can be used for the various applications as a fuel hose without limitation, it is especially suitable for the use as a filler neck hose, the breathing pipe hose of a vapor line, or an evaporation hose.

[0044]

[Example] (Constituent formula of an unvulcanized rubber constituent) In order to prepare the test piece for evaluation concerning each example of examples 1-7 and the examples 1-10 of a comparison concerned in Table 1 - 3 of a test, respectively The following basic combination 2 whose following basic combination 1, NBR or BR, and PVC whose acrylic rubber is a polymer are polymers, and the following basic combination 3 whose BRM is a polymer are followed. And in the predetermined example shows in each table, the white hatching agent was blended and each combination formula of the constituent concerning each example was set up.

[0045] Basic combination 1 polymer 100 weight sections stearic acid One weight section azobiscarbonyl One weight section carbon black (CB) A variate plasticizer Variate processing aid One weight section vulcanizing agent variate vulcanization assistant This basic combination 1 is a thing applicable to examples 1-7 and the examples 1-10 of a comparison. *** -- with the above-mentioned "polymer" While using the acrylic ester of the class shown in the applicable column of each table, and as content, the acrylic rubber which is as the amount of ACR showing an applicable content is put into it.

[0046] Basic combination 2 polymer A 100 weight sections zinc oxide Five weight sections stearic acid One weight section azobiscarbonyl Two weight sections carbon black (CB) A variate plasticizer Variate sulfur 0.5 weight sections thiuram system vulcanization-accelerator agent 1.5 weight sections sulfenamide system vulcanization accelerator The 1.5 weight sections.

[0047] This basic combination 2 corresponds to the examples 2-4 of a comparison, and the above-mentioned "polymer" is BRM whose amount of ACN is 50 % of the weight, NBR and PVC which blended 10% of the weight of PVC in the example 3 of a comparison in NBR whose amount of ACN is 45 % of the weight, and NBR-PVC which blended 30% of the weight of PVC in the example 4 of a comparison to NBR whose amount of ACN is 35 % of the weight in the example 2 of a comparison.

[0048] Basic combination 3 polymer 100 weight sections magnesium oxide Three weight sections calcium hydroxide Six weight sections carbon black (CB) 15 weight sections.

[0049] This basic combination 3 corresponds to the example 1 of a comparison, and the above-mentioned "polymer" is "Borac" F85731Q (trade name) by Sumitomo 363 which is the polyol vulcanizing agent internal Baccorubber (BRM) whose Baccor content is 69%.

[0050] Next, although each table is explained collectively as a plasticizer -- example 1-3, 7, the examples 2 and 3 of a comparison, and 5- the "ADREA 808 RS 107 (trade name)" by Asahi Denka

Kogyo K.K. to 7 and 10 In the example 6, the "ADEKA size RS 735 (trade name)" by Asahi Denka Kogyo K.K. DGA was used for the example 8 of a comparison for DCP for the example 9 of a comparison at the example 4 of a comparison in the phr (weight number of copies per polymer 100 weight section) and which shows the "ADEKA size RS 735 (trade name)" by Asahi Denka Kogyo K.K. in a table, respectively. SP value and molecular weight of these plasticizers are also collectively shown in a table.

[0051] Next, as CB, the "Japanese ink rack N130 (trade name)" by Showa Cabot Corp. was used as "PHF" as "HAF" according to the notation of the carbon grade of first Naka in the phr unit which shows "the Carbon 3 (trade name)" by Tokai Carbon Co., Ltd. as "HAF" for "the Cishike 80 (trade name)" by Tokai Carbon Co., Ltd. in a table, respectively.

[0052] Suchimager, as the example of a comparison is shown in a table, it is Sierra Yule as "tate", 10phr restoration of the chlorine "the mistake THON vapor (trade name)" was carried out.

[0053] Moreover, although the basic combination 1 - the basic combination 2 are explained collectively As the antioxidant of the basic combination 1 The "how guard 445 (trade name)" made from Uniqoyl Chem As an antioxidant of the basic combination 2, "DZONICOM 3C (trade name)" or "the non flex time 80 (trade name)" by the elabrade chemistry company As processing aid of the basic combination 1, "montisse toll 870 (trade name)" by the Esso petroleum company As a reactionant oxide of the basic combination 2, "Cal 2 (trade name)" by the Oel chemistry company was used for "cosmosano MAGU 8130 (trade name)" by the cosmosano chemistry company as a calcium hydrazide of the basic combination 3, respectively.

[0054] Furthermore, although the vulcanizing agent kind concerning the basic combination 1 is shown in Table 1 - 1 "CN 23 (trade name)" by DENKI KAGAKI KIDYO K.K. whose "condensate" is an inorganic system vulcanizing agent is here, Having used "PAL knock AB-8 (trade name)" by the Cuchi Shikoku Chemical industrial company which is this vulcanization accelerator, or "EM ARU 1F needle (trade name)" by Kao Corp. is shown. "Peroxide" shows that the "per hena V-40 (trade name)" by Nippon Oil & Fat Co., Ltd. which is a peroxide system vulcanizing agent, or "the photokhiagen (trade name)" by the elabrade chemistry company was used. As a thixotropic system vulcanization-accelerator agent concerning the basic combination 2, company "Nonceler OZ-03 (trade name)" was used as a sulfenamide system vulcanization accelerator using Ouchi Shikoku Chemical "Nonceler UT-C (trade name)".

[0055] The rubber constituent which is not vulcanized concerning each above mentioned example is kneaded with a Hachery mixer and an opening roll according to the combination formula concerning each example. (Preparation of the test piece for evaluation) these rubber constituents -- hot blast vulcanization (an example 5 and the example 1 of a comparison -- the press cure for 150-degrees/Cx 45 minutes --) of 15/150 degree Cent hours of press cure for 150-degrees/Cx 45 minutes The examples 2-4 of a comparison were fabricated with the press cure for 150-degrees/Cx 30 minutes in the shape of a sheet by the thickness of 1mm, and the test piece for evaluation of the shape of a sheet concerning each example was prepared.

[0056] (Evaluation of initial physical properties) the test piece for evaluation concerning each example -- using -- JIS K -- according to 6251 and 6253, (MPa), elongation (%), and hardness (durometer type A) were evaluated in tensile strength as initial physical properties. The result is shown in Table 1 - 3. About these initial physical properties, 10.0 or more MPa and elongation are considered that it is desirable that hardness (HS) is 50-75 for tensile strength 250% or more.

[0057] (Evaluation of gasoline permeability) CLIP using the so-called "Fast C" gasoline using the test piece for evaluation concerning each example -- the transmission coefficient (mg-cm/cm²/day) was measured and low extended gasoline permeability. It is the approach that one side of a test piece is referred to as being immersed in a gasoline here by the "CLIP method" holding a gasoline in the fixture of a predetermined cup configuration, sealing opening (opening area 1cm²) of a cup with the test piece for evaluation of the shape of a sheet of thickness 1 (mm), and making the whole fixture as a teststand.

[0058] Specifically it is in the condition when held the 100ml gasoline in the cup as pretreatment first, 40-degree immersion [one side] for 107 days is performed, and it is taken its whole after [100ml now

gasoline [every] weight W_0 about this gasoline, (mg) is measured and placed. Next, 40-degree immersion [one side] for 100 days is performed in this condition, and it is every whole cup weight W_1 just behind that, (mg) is measured and said transmission coefficient is computed by the formula called transmission coefficient $= (W_0 - W_1) / 30$. Although the computed transmission coefficient is shown in each table, it is thought that it is desirable as this transmission coefficient that it is 40 or less.

[0059] (Evaluation of a low temperature performance) About the test piece for evaluation concerning each example shown in Table 1 - 3, it is 118. By the cold shock embrittlement trial specified to K8861, low-temperature-embrittlement temperature (degreeC) was measured and the result was shown in Table 1 - 3. It is thought that it is desirable as low-temperature-embrittlement temperature that it is below -20-degreeC.

[0060] (Evaluation of volume resistivity) About the test piece for evaluation concerning each example shown in Table 1 - 3, it is 118. According to J6911, the test method which set applied voltage to 1-100V estimated the volume resistivity value (ohm-cm), and the result was shown in Table 1 - 3 with it. It is thought that it is desirable as a volume resistivity value that they are 108 or less ohm-cm.

[0061] (Heat-resistant evaluation) About the test piece for evaluation concerning each example shown in Table 1 - 3, the elongation change after 120-degree treatment of 168 hours (%) was measured, and the result was shown in Table 1 - 3. It is thought that it is desirable as an elongation change that it is less than -30%.

[0062] (Evaluation of fuel oil-proof nature) About the test piece for evaluation concerning each example shown in Table 1 - 3, the volume change (%) after being immersed in the so-called "Fuel" on the conditions of 40-degreeC x 48 hours was measured, and the result was shown in Table 1 - 3. It is thought that it is desirable as a volume change that it is 30% or less.

[0063] (Evaluation of some gas-proof nature) About the test piece after carrying out two-cycle immersion on the conditions of 40-degreeC x 70 hours at the above "Fuel" which contains 2.5% of the weight of hydrogen peroxide about the test piece for evaluation concerning each example shown in Table 1 - 3, it evaluated whether there would be any abnormalities, such as hardening and softening, and the result was shown in Table 1 - 3. That that "O.K." was written wrote abnormality nothing and "NG [that]" wrote together the contents of the abnormality with abnormalities. The thing with desirable it being "with no abnormalities" cannot be overemphasized.

[0064] (Evaluation of carbon-proof nature) About the test piece after being immersed in the above "Fuel" containing the dicumylperoxide solution of 0.005 mole / L on the conditions of 40-degreeC x 72 hours about the test piece for evaluation concerning each example shown in Table 1 - 3, it evaluated whether there would be any abnormalities, such as hardening and softening, and the result was shown in Table 1 - 3. That that "O.K." was written wrote abnormality nothing and "NG [that]" wrote together the contents of the abnormality with abnormalities. The thing with desirable it being "with no abnormalities" cannot be overemphasized.

[0065] (Evaluation of ozone resistance) About the test piece for evaluation concerning each example shown in Table 1 - 3 After performing pretreatment referred to as presenting the vacuum drying of 40-degreeC x 48 hours after being immersed in "Fuel" on the conditions of 40-degreeC x 48 hours, this test piece in the condition of having made it elongating 40% it was exposed in the bath of the concentration of the ozone of 40-degreeC and 50pphm for 168 hours, it observed whether there would be any generating of a crack, and the result was shown in Table 1 - 3. That "O.K." was written shows that there was no generating of a crack, and, of course, this [is] is desirable.

[0066] (Color evaluation) About the test piece for evaluation concerning each example shown in Table 1 - 3, the condition on the front face of a sheet after leaving it for one week in ordinary temperature was observed after vulcanization, and the existence of bleeding was investigated. That in which the thing without bleeding has "O.K." and bleeding was indicated in the table as "NG."

[0067] Moreover, it judged synthetically whether there would be any problem in workability by Barbary and roll workability, and tensile extension nature about the test piece for evaluation concerning each example shown in Table 1 - 3. That in which what does not have a problem in workability has

[illegible]

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